

SULFUR CHARACTERIZATION IN ASPHALTENE, RESIN, AND OIL FRACTIONS OF TWO CRUDE OILS

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Sulfur chemical species have been determined for asphaltene, resin, and oil fractions of two crude oils by using X-ray absorption near-edge structure (XANES) spectroscopy. The prevalent sulfur species are thiophene, sulfide, and sulfoxide. The asphaltene fraction of one of the oils, CAL, is known to have a very high sulfoxide content. The asphaltene fractions of both the crude oils were analyzed several years ago, and had generated similar sulfur fractions as the present study. This shows that the oxidation of the sulfides in CAL occurred within the earth formation, and not by air oxidation after the production of the crude oil. This also confirms the robustness of the analysis method. Results from this study also show that large sulfoxide fractions are obtained for *all* components of CAL, even in the (typically) non-polar oil fractions. The second crude oil is lower in oxygen, and shows similar composition in *all* three fractions.

Key Words: Sulfur, XANES, Asphaltenes

INTRODUCTION

Crude oils are described as consisting of three fractions—asphaltenes, resins, and oils; these fractions are determined by solubility classification.¹⁻³ One definition is that the oil fractions are the pentane-soluble portion of crude oils, resins are pentane-insoluble and heptane-soluble portions and asphaltenes are heptane-insoluble portions of crude oil. The solubility classification of these crude oil components correlates strongly with chemical properties of the derived components. For instance, asphaltenes from different crude oils are remarkably similar in their chemical properties. Asphaltenes interfere with producing, transporting, and refining of crude oils, and the resins stabilize the suspension of asphaltenes in crude oils; they are, therefore, both prominent in crude oil utilization. Asphaltenes and resins contain higher fractions of heteroatoms, compared to the oil fraction. Consequently, heteroatoms, particularly their polar moieties, partly determine the chemical properties of these crude oil fractions, and, to the extent that solubility is influenced, partly define these fractions. For example, chromatographic studies have shown that certain alkyl sulfides are present in the resin fraction, while the corresponding sulfoxides are present in the asphaltene fraction. The much greater polarity of the sulfoxide group moves the oxidized component from the resin to the asphaltene fraction. The object of this paper is to investigate the relative abundances of the different sulfur chemical forms, especially the polar groups, in the different fractions. The asphaltenes had been studied by the same method about a decade ago, and the present study verified the reproducibility of the results.

XANES spectroscopy has been successfully employed to probe the chemical nature of sulfur in different fossil-fuel components³⁻¹⁰ such as asphaltenes^{3,5,6}, crude oils^{3,7}, and coals^{3,8,9}. Generally, each different chemical form of sulfur gives rise to its own characteristic single, large peak (1s-3p electronic transition). The resonance peaks of sulfide and thiophene are resolvable but are close, introducing some errors in their fractions. The sulfoxide peak, however, is well resolved from all others, and has less associated errors. In asphaltenes, sulfur occurs as mostly thiophenic (aromatic) and sulfidic (saturated) forms. Sulfoxide is the oxidized form of sulfur found in asphaltenes, and usually appears to have resulted from oxidation of sulfide present in crude oils. In some asphaltenes, thiophenic sulfur dominates, while in others, thiophenic and sulfidic forms are comparable. More thermally matured crude oils have prominent thiophenic fractions in the asphaltene fractions. In coal sulfur exists in both organic and inorganic forms. Many coals contain pyrite, and the lowest rank coals may contain sulfate. The organic forms of sulfur in coals are in thiophenic and sulfidic forms, similar to asphaltenes except that coals lack sulfoxides. Nitrogen has also been explored in XANES studies on asphaltenes and other carbonaceous materials.³ These studies have shown that in asphaltenes nitrogen occurs almost entirely in aromatic forms,

in pyrrolic and pyridinic structures.

In this study, we present results of sulfur XANES spectroscopy on asphaltenes, resins, and oil fractions obtained from two crude oils. One of the two asphaltenes is known to be high in sulfoxide, the other low, thus the two crude oils constitute a good test case for the deposition of polar sulfur chemical groups in different crude oil fractions. The asphaltene fractions from both the crude oils had been analyzed by XANES method several years ago, and one of the issues this paper addresses is to verify the robustness of the analysis method, as well as to investigate if there is any considerable air oxidation. In both the studies, XANES sulfur spectra were analyzed with the use of reference spectra of model compounds in the usual fashion.³ The principal finding here is that the three components of the crude oils have similar fractions of sulfoxide. The very polar sulfoxide group does not alter solubility sufficiently to transfer all sulfoxide-containing molecules to the heavy ends.

EXPERIMENTAL

Sulfur K-edge XAFS spectra were collected at beam-line X-19A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. A double-crystal monochromator of Si (111) crystals was used for dispersion. In order to minimize effects from higher order harmonics, about 80% detuning were used. The X-ray beam exited the UHV through a beryllium window immediately adjacent to the sample chamber, which was filled with helium in order to ensure minimum X-ray absorption by the atmosphere. The data were collected in the fluorescence mode with the use of a Stern-Heald detector and Mylar films were used in the sample chambers to hold the sample.

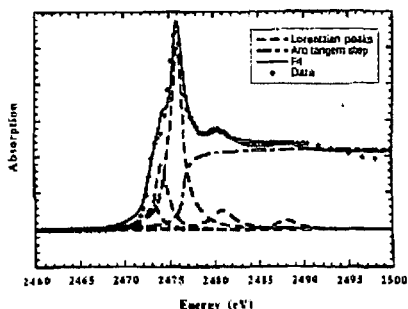
The sulfur model compound samples were first diluted in boric acid, finely ground, and then smeared on sulfur-free Mylar film, which was placed in the beam path. The fossil fuel samples were either ground and mounted on the film, or diluted in CCl₄ and evaporated to dryness on a film that was then placed in the beam path.

All the sulfur models were obtained from Aldrich Chemical Company; they were dibenzyl sulfide, dibenzothiophene, thianaphthene, dibenzyl sulfoxide, iron (II) sulfide, potassium sulfate, and sodium thiosulfate. The fossil-fuel samples were the asphaltene, resin, and oil fractions obtained from CAL and KUW2 (UG8) crude oils.

Virgin stock-tank crude oils CAL and KUW2 were used for analysis. Samples were prepared as follows: a solution was prepared with 40 cc of pentane per gram of crude oil. The solution was stirred for 24 h and filtered. The filtered soil was washed with pentane until the pentane wash was colorless. Pentane was removed from the filtrate by evaporation to yield the oil fraction. The separated solid was dissolved in a small volume of toluene; heptane was then added in the volume ratio of 40: 1. After being stirred for 24 h, the asphaltenes were filtered, and the heptane solution was taken to dryness to obtain the resins. We note that in the non-unique definitions of crude oil components, one could label all pentane-insoluble as asphaltenes. According to this classification, our three fractions would be the heavier asphaltene fraction (heptane-insoluble), the lighter asphaltene fraction (pentane-insoluble and heptane-soluble) and the maltenes. This classification was noted to help comparisons with other work.

A least-squares fitting program was used to quantitatively analyze the sulfur spectra. The spectra were analyzed by methods previously described⁸. The spectra of models and the fossil fuels were first normalized with respect to the step heights and then fitted to a sum of several Lorentzian peaks and an arctangent step. The Lorentzian peaks correspond to resonant electronic transitions,

Figure 1



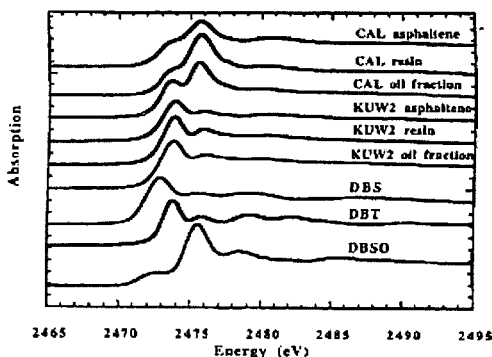
whereas the step accounts for electronic transition to the continuum. The curves from the model compounds were used as basis vectors to fit the curves of the crude oil components. Concentration corrections were applied to the model spectra. Figure 1 illustrates the fitting procedure of a typical sulfur XANES

spectrum, here a spectrum for CAL resin. The fitting procedure was performed on a Macintosh computer using the curve-fit routine of KaleidaGraph software. Using this procedure, all the XANES spectra of the models and the crude oil fractions were fitted. The spectra of the crude oil fractions were then represented as a linear sum of the spectra of model compounds in order to generate sulfur fractions. The error for the sulfide and thiophene fractions is about 10% due to the close proximity of their peaks and the error is smaller for the sulfoxide and higher oxide fractions, which all have isolated peaks.

RESULTS AND DISCUSSION

Figure 2 is a plot of the sulfur XANES of the asphaltene, as well as resin and oil fractions

Figure 2



obtained from CAL and KUW2 crude oils. All these spectra have been normalized to the same step height. In addition, Fig. 2 shows the spectra of dibenzyl sulfide, dibenzothiophene, and dibenzyl sulfoxide, the three relevant model compounds. The model compounds show the dramatic effect that oxygen has on the energy of the $1s-3p$ resonance; higher oxidation states of sulfur yield higher transition energies. The

thiophene and sulfide both have a formal oxidation state of zero, but the thiophene is at a slightly higher energy. This is probably due to effects of aromatic electron delocalization.³ Some electron density in the sulfur lone-pair p_z orbital is delocalized in the ring, thereby reducing electron density on the sulfur site. This effect is very large on nitrogen in the more aromatic pyrrole rings.³

The most striking difference between the two suites of oil component data is seen in the relative intensities of the oxidized (sulfoxide) and reduced sulfur resonance's. For *all* components of the CAL crude oil, the sulfoxide peak dominates. In *all* KUW2 fractions, the sulfoxide is a minor component and reduced sulfur species dominate. The spectra immediately show that sulfoxide is present in approximately the same amounts in all the three components for each crude oil and is not limited to the more polar resin and the asphaltene fractions.

Table I. Relative abundances of sulfur forms in the asphaltene, resin, and oil fractions of CAL, and KUW2 (UG8).

	Sulfide	Thiophene	Sulfoxide	Sulfone	Sulfate
CAL Asph	15	29	50	5	1
CAL Resin	11	27	59	1	1
CAL Oil	24	27	46	1	1
KUW2 Asph	40	55	2	1	1
KUW2 Resin	40	52	5	1	1
KUW2 Oil	45	47	5	1	1

The relative abundance's of the different sulfur forms of the asphaltenes, resins and oil fractions obtained from CAL and KUW2 crude oils is tabulated in Table I. These samples are not expected to have any sulfone or sulfate, and, within error, which is estimated to be within 10%, none was found. All the fractions of CAL and KUW2 show considerable fractions of organic

sulfide and thiophene. In addition, all fractions of CAL contain high and comparable quantities of sulfoxide. Asphaltenes and resins are known to be more polar than the oil fraction; moreover, sulfoxide is very polar. In spite of this observation, the oil fraction of CAL contains a high fraction of oxidized sulfur. Of course, sulfur represents a smaller mass fraction of the oil phase than of the heavier ends. The resin fraction of CAL has a greater sulfoxide fraction than the asphaltene fraction does, perhaps making the resins the most polar fraction for this crude oil. The sulfur compositions of the KUW2 fractions are all low in sulfoxide and are also comparable in their sulfide and thiophene fractions. For both CAL and KUW2, the oil fractions have slightly higher sulfide fractions. Similarly, the carbon in the oil fraction is also less aromatic in the oil fraction than in the heavy ends.¹⁻³

Table II. Results from XANES analysis by Waldo et al.⁷

Asphaltene	Sulfide	Thiophene	Sulfoxide	Sulfone	Sulfate
CAL	16	36	44	3	<1
KUW2	43	52	4	2	<1

Previously, asphaltene fractions from CAL and KUW2 were studied by Waldo et al. by XANES spectroscopy, and yielded similar results, as shown in Table II⁷, in spite of the seven-year difference in the isolation and analysis of the different CAL and KUW2 asphaltene samples. Error analysis performed on the analysis procedure confirms that the above analysis method is robust, and the numbers are within a 10% error margin. The present study also confirms that the most likely source of sulfoxide is oxidation of the sulfide *within* the crude oil,⁶ which is consistent with the well-known lability of some sulfides towards oxidation. A stock tank oil sample was used for the experiments, and not a sealed-bottom-hole sample. Therefore, it is unlikely that the sulfoxide in CAL was generated after production of the crude oil by air oxidation. We have treated all our asphaltene and crude oil samples in a similar manner, yet CAL asphaltene has a sulfoxide fraction four times greater than any other we examined,⁶ while the KUW2 asphaltene has little sulfoxide. Furthermore, the CAL resin and the CAL oil phase contain large sulfoxide fractions, while the corresponding KUW2 fractions show little sulfoxide in spite of identical treatment of these crude oil samples. Thus, we believe that the extreme oxidation of the sulfides in CAL occurred within the earth formation, perhaps due to contact with meteoric water. The small thiophene fraction in CAL is consistent with low maturity, the shallow depth of burial allowing for exposure to meteoric water.

CONCLUSIONS

Sulfur XANES analysis shows that the sulfoxide-to-sulfur ratios are comparable in all fractions of a given crude oil. Sensitivity analysis confirms the robustness of the XANES analysis method, previous results were similar, in spite of the seven-year difference in the isolation and analysis of the different CAL and KUW2 asphaltene samples. This study also supports the contention that the oxidation process took place *in situ*; thus, the sulfur speciation of different virgin asphaltenes and crude oils can be very different in nature, with sulfoxide fractions varying from 0 to 50%. Such large variations in the chemistry of different petroleum asphaltenes are unusual. These results should be considered when comparing asphaltene results from different studies and samples, because sulfoxides are very polar and thereby partly determine the asphaltene fraction.

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